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Valence Bond Glass on an fcc Lattice in the Double Perovskite Ba_2YMoO_6

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We report on the unconventional magnetism in the cubic B-site ordered double perovskite Ba_2YMoO_6, using ac and dc magnetic susceptibility, heat capacity and muon spin rotation. No magnetic order is observed down to 2 K while the Weiss temperature is ~ -160 K. This is ascribed to the geometric frustration in the lattice of edge-sharing tetrahedra with orbitally degenerate Mo^{5+} $s = 1/2$ spins. Our experimental results point to a gradual freezing of the spins into a disordered pattern of spin singlets, quenching the orbital degeneracy while leaving the global cubic symmetry unaffected, and providing a rare example of a valence bond glass.

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Magnetic insulators with lattices in which antiferromagnetic (AF) bonds are geometrically frustrated have been studied widely in the pursuit of exotic quantum ground states such as spin liquid [1,2]. Such nonclassical ground states have mainly been sought in low dimensional structures such as the triangular lattice system κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ [3] and the kagome antiferromagnet herbertsmithite [4]. Materials with a geometrically frustrated face centered cubic (fcc) lattice have in this respect received much less attention. The 12 near-neighbor magnetic bonds J_1 between the [000] and $[\frac{1}{2}\frac{1}{2}0]$ spins on the fcc lattice form a network of edge-sharing tetrahedra (Fig. 1). When these bonds are AF ($J_1 > 0$) the magnetism is geometrically frustrated, giving rise to a large (but not macroscopically large [5] as for the kagome lattice) ground-state manifold of spin configurations unrelated by symmetry. Further neighbor interactions (J_2) along the 6 [100] vectors lift this degeneracy only partially; $J_2 < 0$ (along the 6 [100] vectors) leads to type I order, weak AF exchange ($0 < J_2 < 2J_1$) to type III order and stronger AF exchange $J_2 > 2J_1$ to type II order. Thermal or quantum fluctuations and quenched disorder have been shown to result in a bias for respectively collinear and anticollinear states within these degenerate ground-state manifolds [6–8], an entropic selection effect termed ''order from disorder'' [9]. This is in agreement with experiments on well-known compounds of rocksalt structure such as MnO [10,11], $Cd_{1-x}Mn_xTe$ [12], and NiO, MnSe [10]. Classical type I, II or III order has also been confirmed for $s = 1/2$ [13–15] although less is known about the physics at the boundaries between the classical phases. In this Letter we describe the unconventional magnetism in the compound Ba_2YMoO_6, providing experimental evidence that an exotic valence bond glass (VBG) [16,17] state can stabilize at the boundary between the known classical phases on the fcc lattice. Such a disordered state has been predicted to be possible even in the absence of structural disorder, as an example of a nonequilibrium quantum ground state [16].

The B-site ordered double perovskites are of general stoichiometry $A_2BB'O_6$ where the A site typically hosts alkaline-earths and lanthanides and the B sites can host $3d$, $4d$, and $5d$ transition metal (TM) ions. Depending on the combination of B and B' site ions, electronic phases from strongly correlated metals via half-metals [18] and semiconductors [19,20] to Mott insulating can be realized. Mott insulating $4d$ and $5d$ TM compounds are rare. The occurrence of this insulating phase in the double perovskites is due to the large distance between the TM ions, of the order of 5 to 6 Å. Examples of Mott insulators are Ba_2LaRuO_6 and Ca_2LaRuO_6 [21], respectively, type III and type I antiferromagnets. Sr_2CaReO_6 [22] and Sr_2MgReO_6 [23] (the Re^{6+} has $s = 1/2$) have spin-glass ground states, consistent with a negligible J_2 along the pathway Re-O-B'-O-Re. There is a large group of Mo^{5+} compounds Ba_2LnMoO_6 with Ln = Nd, Sm, Eu, Gd, Dy, Er, Yb and Y [24]. The Mo^{5+} has a singly-occupied $4d$ t_{2g} level with $s = 1/2$. Because of the strong spin-orbit coupling in $4d$ TM ions in a cubic crystal field this is expected to lead to a $j = 3/2$ triplet [25,26]. Only the larger lanthanide compounds

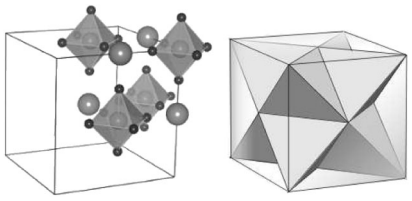

FIG. 1. Four MoO_6 octahedra (shaded grey) and Y ions (large spheres) in the cubic unit cell of Ba_2YMoO_6 (left). The Mo^{5+} ions form a lattice of edge-sharing tetrahedra (right). The cubic lattice constant is 8.389 Å.

(Ln = Nd, Sm and Eu) have Néel order (Type I, implying $J_2 < 0$) coinciding with a weak Jahn-Teller distortion [24,27,28], while the exchange interaction is of the order of 100 K [24]. The other compounds were found to be paramagnetic and with cubic symmetry at all temperatures. Ba_2YMoO_6 is the simplest of these compounds because the Y^{3+} ion does not carry a magnetic moment. The magnetic exchange is mainly via the 90° B'-O-O-B' $\pi - \pi$ bonds [21,24], giving rise to 12 near-neighbor AF J_1 bonds for each spin, across the edges of the tetrahedra (Fig. 1).

Polycrystalline Ba_2YMoO_6 was prepared by the solid state reaction of stoichiometric oxides of Y_2O_3, MoO_3 and $BaCO_3$ powders of at least 99.99% purity. These were ground, die-pressed into a pellet and heated under flowing 5% H_2/N_2. The final synthesis temperature was 1200–1250 °C with three intermediate regrinding steps to ensure phase homogeneity. It was found that a first heating step of ~2 hr at 900 °C in air and thorough homogenization helps to prevent the formation of $BaMoO_4$ and Y_2O_3 impurities. Phase purity was confirmed by laboratory x-ray powder diffraction. In a related paper [29] neutron powder diffraction results are discussed, which show that the Y/Mo site disorder is less than 1%. The diamagnetic analog, Ba_2YNbO_6, was prepared at 1200 °C in air from $YNbO_4$ and $BaCO_3$. The sample magnetization was measured on a Quantum Design magnetic property measurement system (MPMS) in fields up to 5 T. The heat capacity was measured on a Quantum Design physical property measurement system (PPMS), using 7.0 mg of a sintered pellet. The μSR experiment was carried out at MUSR at ISIS, UK.

The dc magnetic susceptibility measured in a 1 T field is shown in Fig. 2. A Curie-Weiss fit to the high temperature susceptibility yields a Weiss temperature of −160 K and a Curie constant of 0.25 emu mol^{-1} K^{-1}, small compared to the 0.38 emu mol^{-1} K^{-1} expected for $s = 1/2$. This difference is attributed to strong quantum fluctuations common in low-spin antiferromagnets and previously observed in double perovskites [26]. Below 25 K a second linear regime is observed in χ^{-1}, corresponding (for a 1 T field) to a ~10% fraction of all the $s = 1/2$ moments (or ~5% if they have the full $j = 3/2$ where $g_J = 4/3$) and a Weiss temperature of −2.3 K indicating weak AF exchange. This fraction is too large to be ascribed directly to either structural disorder or an impurity phase in the sample. Furthermore, fits to $M(H)$ measured at 2.3 and 5 K (inset of Fig. 2) with Brillouin functions lead to estimates of, respectively, 2% and 7% of all spins, compared to 10% for fits to the $M(T)$ curve. This suggests that the apparently quasifree spins are an emergent property of the (disorder free) system.

The ac susceptibility measured with a field amplitude of 5 Oe and zero dc offset field is shown in Fig. 3. The dispersive part of the ac susceptibility (χ') is almost frequency independent and is comparable to the diverging low-temperature dc susceptibility. The dissipative part (χ'') shows a frequency dependent maximum between 26 and 70 K. Remarkably, the maximum gradually gets sharper as the frequency increases, instead of weaker as expected for a spin-glass transition. The agreement between the dc susceptibility and χ' below 20 K is a strong indication that the Curie term can be ascribed to the weakly-coupled spins.

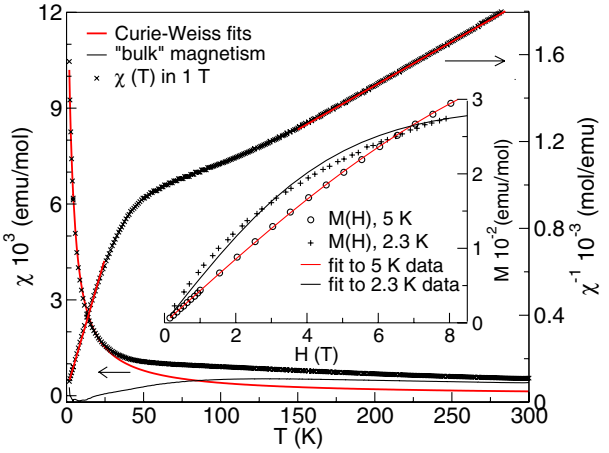

FIG. 2 (color online). The dc magnetic susceptibility χ (x, left axis) and χ^{-1} (x, right axis) of Ba_2YMoO_6 measured in 1 T. Curie-Weiss fits in the two linear regimes in χ^{-1} are indicated in grey (red) and the black line gives the difference between the total susceptibility and the low-temperature Curie term. The inset shows $M(H)$ at 2.3 (+) and 5 K (○) and fits to the data with Brillouin functions, accounting for 7% of the Mo $s = 1/2$ spins at 5 K but only for 2% at 2.3 K.

The heat capacity associated with the single Mo^{5+} $4d$ electron in Ba_2YMoO_6 (as shown in Fig. 4) was obtained from comparison with the heat capacity of the diamagnetic analogue Ba_2YNbO_6. The heat capacity from phonons of Ba_2YMoO_6 is expected to be lower than for Ba_2YNbO_6 by a factor 0.991 due to the mass difference between the Mo and Nb nuclei. However, this is small compared to the experimental error in the sample mass which is known with

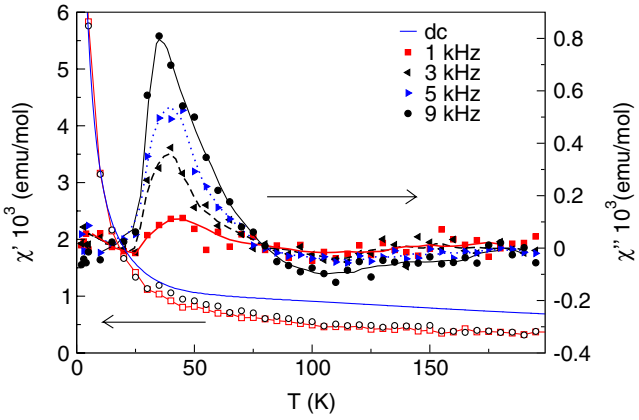

FIG. 3 (color online). The temperature dependence of the dispersive (left axis, open symbols) and dissipative (right axis, filled symbols) components of the ac susceptibility. The solid lines are guides to the eye.

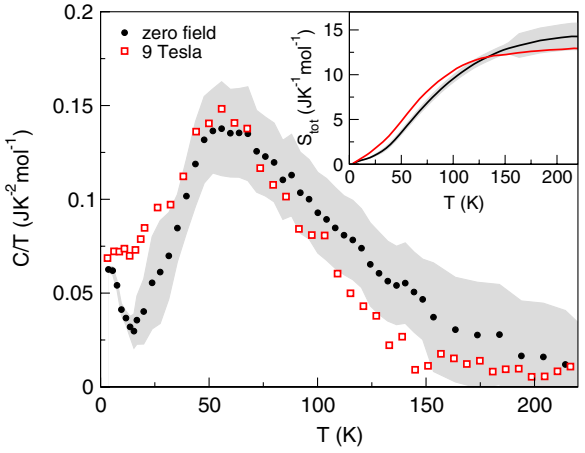

FIG. 4 (color online). The magnetic heat capacity obtained by subtracting the heat capacity of the diamagnetic analogue Ba_2YNbO_2 in zero field (black dots) and in 9 Tesla (open squares). The experimental error for the 9 T data is comparable to that indicated for the zero-field data (grey area). The inset shows the total entropy release as a function of temperature in zero field (black line) and in 9 T (red line).

10% accuracy. For this reason the heat capacity was measured well into the paramagnetic regime and matched to the heat capacity of Ba_2YNbO_6 above 200 K (150 K) for the zero-field (9 T) measurements [30]. The magnetic entropy is gradually released over a wide range of temperatures with a broad maximum around 50 K. No anomalies corresponding to phase transitions are observed, only a gradual freezing, quenching all degrees of freedom associated with the orbitally degenerate t_{2g} $s = 1/2$ $4d$ electrons. As shown in the inset of Fig. 4, the total entropy recovered $S_{\rm tot} = 12 \pm 2\ {\rm J\,K^{-1}\,mol^{-1}}$, close to the $R\ln 4 = 11.5$ expected for a $j = 3/2$ quadruplet (the $j = l - s = 1/2$ doublet lies at much higher energies [25,26]). Below 25 K only ~5% of the entropy is released, in agreement with the Curie fit to the low-temperature susceptibility which was found to correspond to ~5% of the Mo^{5+} if these remaining spins have $j = 3/2$. In a 9 T magnetic field most of the magnetic entropy shifts to lower temperatures.

To gain a better understanding of the gradual freezing and the appearance of apparently weakly-coupled spins a μSR experiment was carried out. The zero-field muon spin relaxation spectra at 120 K, 5 K and 1.4 K are shown in Fig. 5. There is no evidence of muon relaxation due to nuclear spins which confirms that the main muon stopping site is near the O^{2-} ions. At 120 K there is no muon relaxation, as expected for a paramagnetic state. Remarkably, at 5 K a muon relaxation is still only just detectable. If the maximum in the ac susceptibility is due to a conventional spin-glass transition a Lorentzian Kubo-Toyabe muon relaxation is expected below the spin-glass transition, as observed in the related system Sr_2MgReO_6 [23]. The very slow muon relaxation observed at 5 K in Ba_2YMoO_6 indicates there are no static moments. At the same time the heat capacity data show that at 5 K most of the magnetic entropy associated with $j = 3/2$ is quenched, implying static order. The majority of spins must therefore have bound into (nonmagnetic) static spin-singlet "valence bonds" in which also the orbital degrees of freedom are quenched. The moderate increase in the muon relaxation rate below 5 K is then due to slowing-down of a small fraction of the spins which are left isolated as domain walls or defects in a (disordered) valence bond crystal (VBC). The best characterization of this state is probably a valence bond glass (VBG) as described in Ref. [17].

The magnetic properties of Ba_2YMoO_6 are very different to those of the related compound Sr_2MgReO_6 [23], where a first order transition to a conventional spin-glass state is observed. That the crossover in Ba_2YMoO_6 is not a conventional spin-glass transition is also clear from the unusual frequency dependence of the ac susceptibility. The gradual freezing and crossover region around 50 K are consistent with a pseudogap predicted for the VBG [17]. This gap, which corresponds to a spin-singlet dimerization energy scale, is filled by levels corresponding to emergent weakly-coupled spins which give rise to a diverging susceptibility as the temperature is decreased. In close agreement with Ref. [17] the observed low-temperature susceptibility follows a power law $\chi \propto (T - T_s)^{-\gamma}$ with $\gamma \approx 1$. As noted earlier, this contribution from effectively weakly-coupled spins cannot be related one-to-one to any structural disorder but arises as a cooperative effect, due to the amorphous arrangement of spin singlets. The heat capacity does not become zero at the lowest temperature measured which is consistent with a small residual entropy and an ungapped spectrum as expected for the VBG.

The classical ground-state energy is highest when $J_2 \approx 2J_1$, at the crossover between type III ($J_2 < 2J_1$) and type II magnetism (the energy per spin is $-J_1/2 + J_2/4$ for $J_2 \leq 2J_1$). One possibility is that around this crossover a spin-singlet state is energetically favored. A complete explanation of why spin singlets stabilize will in the

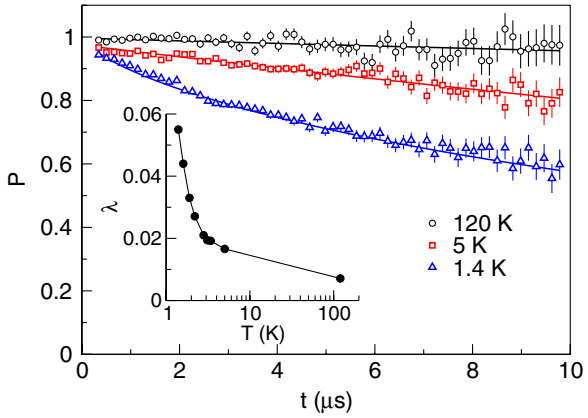

FIG. 5 (color online). The muon spin relaxation at 120, 5 and 1.4 K. The relaxation follows an exponential decay ($P(t) = \exp[-t/\lambda]^{\beta}$, solid lines) with $\beta = 1$ for all but the 1.4 K data, where $\beta = 0.7$. The temperature dependence of the relaxation rate λ is shown in the inset.

present case also involve the orbital degrees of freedom; it is the valence-bond formation rather than a Jahn-Teller effect that fixes the orbital orientation. This could be accompanied by local structural distortions which do not lead to experimentally observable [24,29] structural changes because the valence bonds do not form a regular pattern within the crystal. As first observed by Goodenough and Battle [21], the band width is an important factor in understanding the magnetism in double perovskites with $4d$ and $5d$ transition metal ions. Because Ba_2YMoO_6 is a relatively wide-band insulator it could also be that the stability of a spin-singet state can be understood in terms of the $t - J$ model [31].

In conclusion, the B-site ordered double perovskite Ba_2YMoO_6 has Mo^{5+} ions with a singly-occupied degenerate t_{2g} orbital in a cubic crystal field and with $s = 1/2$. These moments are located on an fcc lattice and coupled antiferromagnetically, with a Weiss temperature of -160 K. At high temperature the single-ionic $j = 3/2$ moments are strongly reduced by quantum fluctuations, consistent with the formation of stable spin-singlet dimers at low temperatures. Remarkably, the dimerization pattern appears to be disordered, giving rise to emergent effectively unpaired spins with a diverging susceptibility as the temperature is reduced, in agreement with theoretical predictions of a VBG [17]. It is proposed that the stabilization of spin singlets is a result of the fine-tuning of the ratio J_2/J_1 to the boundary between the classical type II and type III phases. Clearly the present results provide a strong motivation for further theoretical explorations of the phase diagram of the fcc antiferromagnet and of the interplay between spin and orbital degrees of freedom in $4d$ and $5d$ transition metal compounds. This is the first observation of a VBG in a quantum magnet. Further experimental studies are needed to understand the relationship between the structural and magnetic disorder in this class of materials.

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Note added.—After submission of this Letter a paper on Ba_2YMoO_6 by Aharen *et al.* [32] has appeared. Their conclusions are broadly in agreement with our observations.

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